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ISOLATION AND DETERMINATION OF NORMAL HEPTANE AND OF METHYLCYCLOHEXANE IN A MIDCONTINENT PETROLEUM

(INCLUDING A DETERMINATION OF THE PHASE EQUILIBRIUM DIAGRAM FOR THE CONDENSED SYSTEM NORMAL HEPTANE-METHYLCYCLOHEXANE)^{1 2}

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ABSTRACT

An Oklahoma petroleum was fractionated by distillation into a series of 1° cuts. After removal of the toluene from the fractions boiling between 93° to 101°C., by nitration, and subsequent fractional distillations, most of the heptane and the methylcyclohexane were found to concentrate in the fractions boiling between 98° and 100°C. Both of these hydrocarbons were isolated in a practically pure condition by further distillation through a 35-foot laboratory column. For the final fractionation of the material by equilibrium melting a specially designed freezing apparatus and a centrifuge adapted for low-temperature work were used.

The following physical constants were determined for the isolated *n*-heptane and methylcyclohexane: Specific gravity, refractive index, boiling point, freezing point, aniline point, and molecular weight. Photographs were also taken of the infra-red absorption spectrum of the isolated hydrocarbon. The purity of both compounds was calculated to be above 99.8 mole per cent. Based upon the crude petroleum, it was found that not less than 0.9 per cent of *n*-heptane and not less than 0.3 per cent of methylcyclohexane are present.

It was found that, contrary to a statement in the literature, a constant boiling mixture of *n*-heptane and methylcyclohexane is not formed and hence that a complete separation of the mixture is possible by distillation alone.

The phase-equilibrium diagram for the condensed system *n*-heptane-methylcyclohexane was determined and the eutectic mixture corresponding to about 93 weight per cent of methylcyclohexane was found to freeze at -130.3° C.

CONTENTS

	Page
I. Historical.....	526
1. <i>n</i> -heptane.....	526
2. Methylcyclohexane.....	526
II. Methods employed and apparatus used.....	527
III. Experimental procedure and results.....	529
1. Preliminary distillation of the crude petroleum and subsequent removal of the toluene.....	529
2. Further fractionation of the material and preliminary identification of <i>n</i> -heptane and methylcyclohexane.....	530
3. Isolation of <i>n</i> -heptane and methylcyclohexane.....	533
4. Determination of the freezing point-composition diagram of the binary system: <i>n</i> -heptane-methylcyclohexane.....	534
IV. Discussion of the results.....	534
V. Acknowledgment.....	539
VI. Bibliography.....	539

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I. HISTORICAL

1. *n*-HEPTANE

Although the presence of *n*-heptane in petroleum has been indicated by Schorlemmer (1),⁴ Beilstein and Kurbatoff (2), Charitschkow (3), and others (4) during the earliest stages of petroleum research, the isolation of this hydrocarbon in a pure state from petroleum has been attended with many difficulties. Many investigators (4) have reported the isolation of *n*-heptane from petroleum, but the physical constants of their samples, when given, indicate that in practically every case the material regarded as "heptane" consisted of a mixture of heptane with considerable quantities of naphthene hydrocarbons.

As examples, we may take the heptane samples reported by Warren (5) and by Mabery (6). These samples had boiling points which were nearly the same as that of pure *n*-heptane, but combustion analyses indicated that the carbon-hydrogen ratio was too large to correspond to a pure paraffin hydrocarbon. From this fact as well as from the values which these investigators reported for the vapor density, it is apparent that their samples of "*n*-heptane" were contaminated with considerable quantities of naphthene hydrocarbons.

In more recent years Anderson and Erskine (7) and Brown and Carr (8) have made further attempts to isolate *n*-heptane from petroleum by distillation alone. However, the specific gravity ($d_{15.5}^{15.5} = 0.7117$ instead of 0.6867) given by the former and the refractive index ($n_D^{20} = 1.4068$ instead of 1.3877) given by the latter investigators indicate that their samples also were mixtures of *n*-heptane with naphthenes and possibly with other hydrocarbons. Francis and Young (9) subjected their heptane fractions to treatments with bromine. The resulting monobromides were then fractionated by distillation at reduced pressures after which the *n*-heptyl bromide fraction was reduced to *n*-heptane. In this way a small sample of nearly pure heptane was obtained.

The most recent publication on the isolation of *n*-heptane from petroleum is that of Shepard, Henne, and Midgley (10). These investigators used a combination of distillation and a vigorous treatment with chlorosulphonic acid (11), and were able to isolate the *n*-heptane in an extremely pure condition. While the chlorosulphonic acid method gives a rapid means of obtaining normal paraffin hydrocarbons from petroleum, it could not be employed in the present instance since this reagent not only partially destroys the *n*-heptane, but also completely destroys the branch chain and cyclic hydrocarbons and thus renders impossible their identification and determination in the petroleum.

2. METHYLCYCLOHEXANE

Methylcyclohexane has apparently never been isolated from petroleum in a demonstrably pure condition. However, its presence in different crude petroleums has been indicated by investigators, such as Lachowicz (12), Charitschkow (13), Young (14), Poné (15), Mabery and Sieplein (16), and Markownikoff (17).

⁴ Numbers in parentheses here and elsewhere in the text refer to the bibliography at the end of the paper.

II. METHODS EMPLOYED AND APPARATUS USED

The petroleum fractions used for this investigation were distilled by S. T. Schicktanz and a staff of assistants in rectifying stills of Pyrex laboratory glass. A complete description of the distillation equipment as well as methods of operating the stills has been published in a recent paper (18).

After the preliminary distillations, the toluene was removed from the fractions, boiling between 93° and 101° C., by means of a nitrating

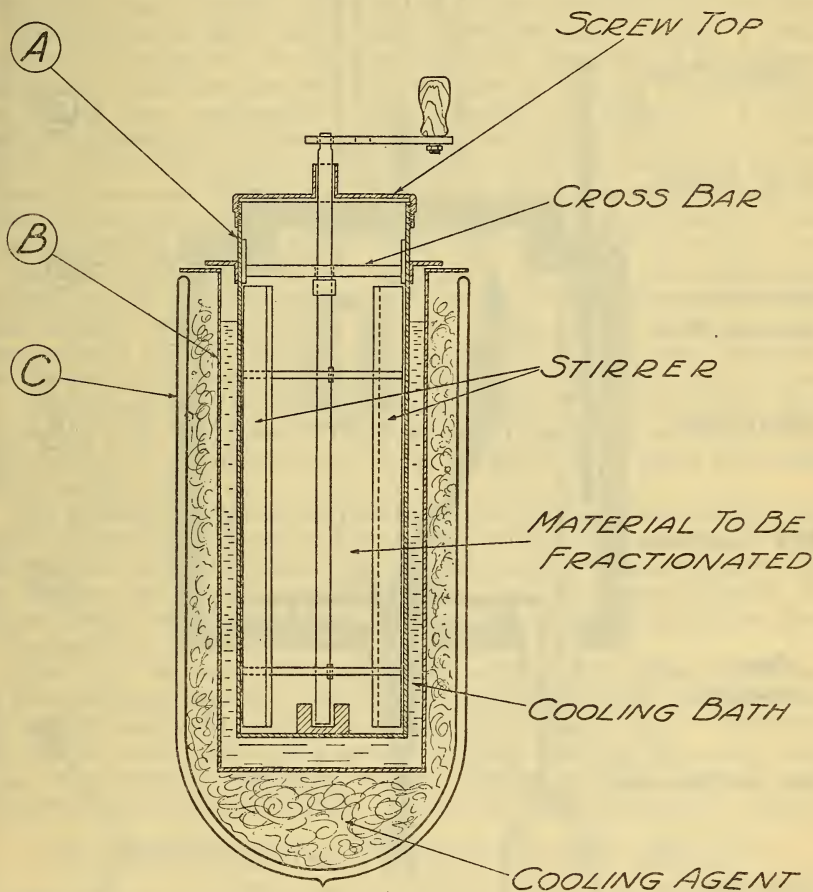


FIGURE 1.—Apparatus for freezing the material to be fractionated by equilibrium melting

treatment previously described (19). After the final distillations, further purification of the heptane as well as of the methylcyclohexane was accomplished by equilibrium melting. For this purpose the material was cooled in a freezing apparatus until a large amount of the solid phase had crystallized out. In this way the impurities were concentrated in the "mother liquor" which was separated subsequently from the pure solid crystals by means of a centrifuge suitable for low temperature work,

The freezing apparatus is shown in Figure 1.⁵ The material to be fractionated was introduced into the brass freezing vessel, *A*, which was provided with a top to prevent condensation of moisture from the air and a stirrer. The freezing vessel, *A*, was placed in a brass cooling

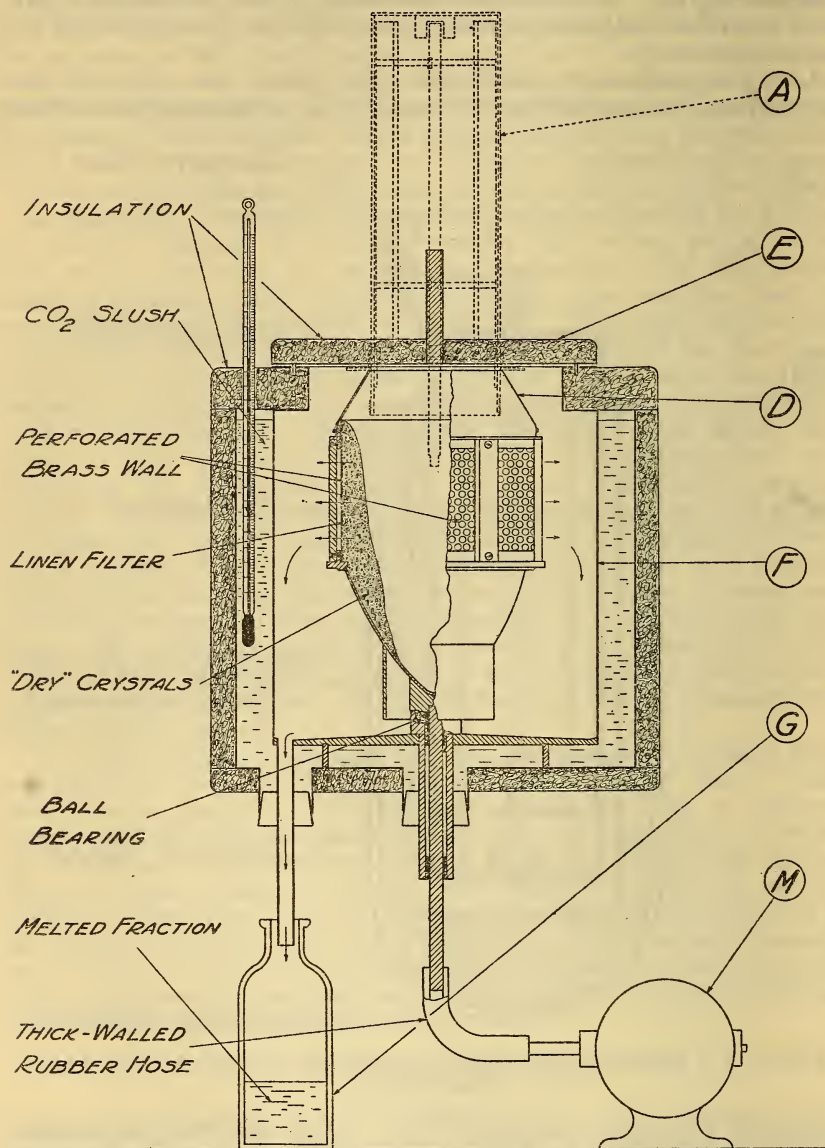


FIGURE 2.—Centrifuge for fractionation by equilibrium melting

bath, *B*, which was filled with a suitable liquid.⁶ The two brass vessels, *A* and *B*, were then placed in a Pyrex Dewar flask, *C*, and cooled. The preliminary cooling, to about -80°C ., was accom-

⁵ Acknowledgment is made to F. W. Rose for drawing all of the figures in this paper.

⁶ For information concerning nonflammable liquid mixtures having low freezing points the reader is referred to a paper by Kanolt (20).

plished by means of a slush of solid carbon dioxide, carbon tetrachloride and chloroform. Further cooling of the petroleum fraction to its freezing point, and finally to solidification, was accomplished by means of liquid air or liquid nitrogen. In order to prevent the material in the vessel, *A*, from freezing to a hard mass, it was necessary to provide constant agitation during freezing. For the same reason, it was desirable to maintain the temperature of the cooling bath only a few degrees below the freezing point of the material to be fractionated. In this way a soft crystalline slush can be obtained easily for materials which contain comparatively large amounts of impurities.

Compounds of fairly high purity, however, have usually a great tendency to supercool and then suddenly to freeze into a hard mass. Because of this fact, the following method of freezing was preferred for nearly pure compounds. The material was placed in a brass cylinder provided with a top (but without a stirrer), then precooled to about -80°C . with carbon dioxide slush, and finally frozen to a hard mass by means of liquid air. The brass cylinder was then removed from the cooling agent and allowed to stand in a Dewar flask until the hard crystalline material began to melt into a soft, but still solid mass.

As soon as this had been accomplished the material was transferred rapidly into the rotating drum, *D*, of the centrifuge (see fig. 2) which had already been cooled to -80°C .⁷ This transfer was made by momentarily placing the freezing apparatus, *A*, in an inverted position on the top of the centrifuge, as indicated by the dotted lines in Figure 2. The frozen material in the rotating drum, *D*, was broken up, and stirred to a uniform mass. Then the centrifuge was covered with the top, *E*, and the rotating drum, *D*, was set into rapid motion by means of the motor, *M*.

The cylindrical walls in the rotating drum, *D*, in the centrifuge were made of perforated brass and were lined with fine linen cloth. This allowed the melted portion of the crystals, or the "mother liquor," to be thrown out by the rotating motion into the brass cylinder, *F*. From here it passed down into the flask, *G*, and constituted the first "fraction."

The "dry" crystals which remained on the inside wall of the drum, *D* were scraped into the cone-shaped bottom of vessel, *D*, and were allowed to melt into a slush under intermittent agitation. The drum *D*, was rotated again and a second fraction was run off, and so on. The last fraction consisting of the highest melting crystals was removed from the walls and the bottom of *D* with the aid of a spoon.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. PRELIMINARY DISTILLATION OF THE CRUDE PETROLEUM AND SUBSEQUENT REMOVAL OF THE TOLUENE

The crude petroleum used for this investigation was obtained from No. 6 well of the South Ponca Field, Kay County, Okla. The properties as well as the preliminary distillations of the crude oil have been described in previous papers (21) (22). The amounts of material obtained in separate 1°C . cuts are shown in Figure 3. The largest

⁷ The centrifuge shown in Figure 2 is designed primarily for fractionation of compounds having freezing points above -80°C . For mixtures with lower initial freezing points a more efficient separation could be obtained if a liquid air-cooled jacket were placed between the rotating drum *D* and the wall of the brass cylinder *F*. Thus a slower melting of the material placed in the rotating drum *D* could be accomplished and consequently it would be easier to obtain equilibrium conditions between the solid and liquid phases.

amount is shown to have distilled between 98° and 99° C. or around the boiling point of *n*-heptane. After the preliminary distillations, all of the fractions were subjected to a nitrating treatment for the purpose of removing and determining the toluene. The isolation of toluene from these fractions has been described in a previous publication. (19.) After the nitrating treatment the fractions were

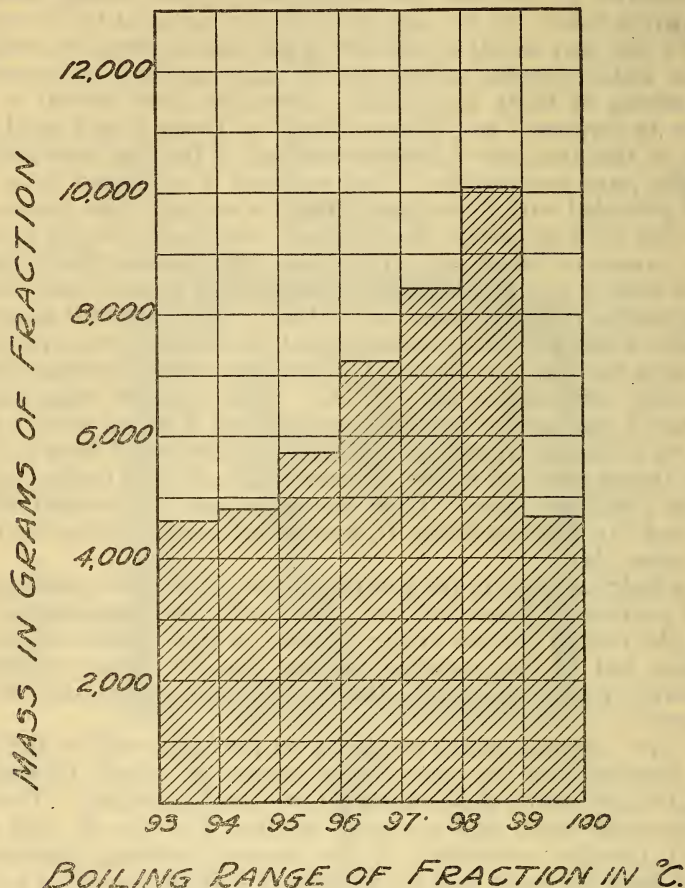


FIGURE 3.—Distribution of the fractions over their boiling range before removal of the toluene

washed with a solution of sodium hydroxide and with distilled water and finally dried over calcium chloride.

2. FURTHER FRACTIONATION OF THE MATERIAL AND PRELIMINARY IDENTIFICATION OF *n*-HEPTANE AND METHYLCYCLOHEXANE

The toluene-free fractions were subjected to further distillations in 30-plate rectifying stills of glass. (18.) Most of the material with boiling points between 93° and 97° was concentrated into two large fractions boiling around 92° C. and around 98° C., respectively. As shown in Figure 4 about 12,500 g of material distilled near the boiling point of *n*-heptane (98° and 99° C.). The initial freezing points and

the refractive indices of the fractions were determined and plotted against their boiling ranges. (See fig. 5.)

From the physical constants of the fractions it was apparent that the mixtures consisted of *n*-heptane and methylcyclohexane. This was confirmed in the following way:

1. A 1,000 g sample of the 98° to 99° cut was agitated with chlorosulphonic acid at 40° C. for eight hours. The acid layer was then replaced with fresh acid after which the mixture was agitated at 40° C.

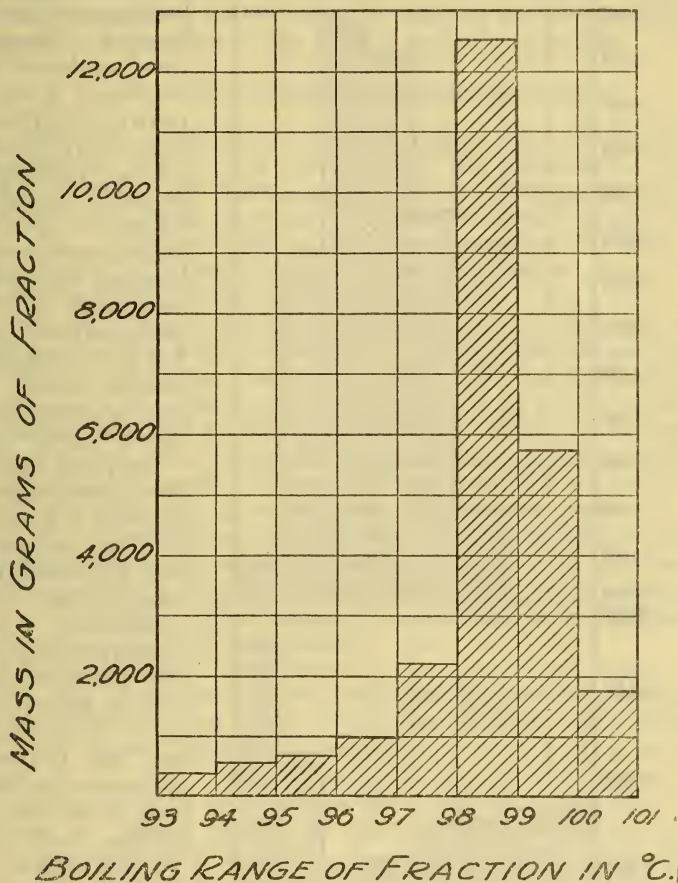


FIGURE 4.—Distribution of the fractions over their boiling range after removal of the toluene and subsequent fractional distillation

for another eight hours. The remaining unattacked hydrocarbon layer was finally washed with sodium hydroxide solution and with water after which it was distilled over sodium hydroxide in a 10-plate bubbling-cap still. The middle portion of the distillates was found to consist of nearly pure *n*-heptane as indicated by its freezing (−90.68° C.), its narrow freezing range and its other physical constants.

2. Another sample of the 98° to 99° cut was passed through a dehydrogenation furnace filled with palladinized asbestos and maintained at about 350° C. The reaction products, which had a distinct odor of toluene, were then subjected to nitration at 5° C., as a result of which a yellow nitroproduct was obtained. This nitroproduct was

identified as, 2, 4-dinitrotoluene, which confirmed the formation of toluene by dehydrogenation of the fraction. Because of this fact the 98° to 99° cut must have contained dihydrotoluene, tetrahydrotoluene, or methylcyclohexane (hexahydrotoluene). The zero iodine number of the fraction excluded the possibility of di- or tetrahydrotoluene. Thus methylcyclohexane must have been a constituent of the 98° to 99° cut.

Having identified the constituents of the mixture the problem of their isolation at first appeared rather complicated because a constant boiling mixture of *n*-heptane and methylcyclohexane has been reported (23). In view of this fact the following methods of separation were tried: (a) Equilibrium melting (21), (b) distillation with alcohols (24), (c) extraction with aniline (25), and (d) extraction with SO₂ (26).

While none of these methods alone would give a sharp separation

it was found that a combination of equilibrium melting and of distillation with methyl or ethyl alcohol gave a fairly good separation. Thus it was possible to obtain a small sample of methylcyclohexane, the freezing point and other physical constants of which indicated a purity of above 98 mole per cent.

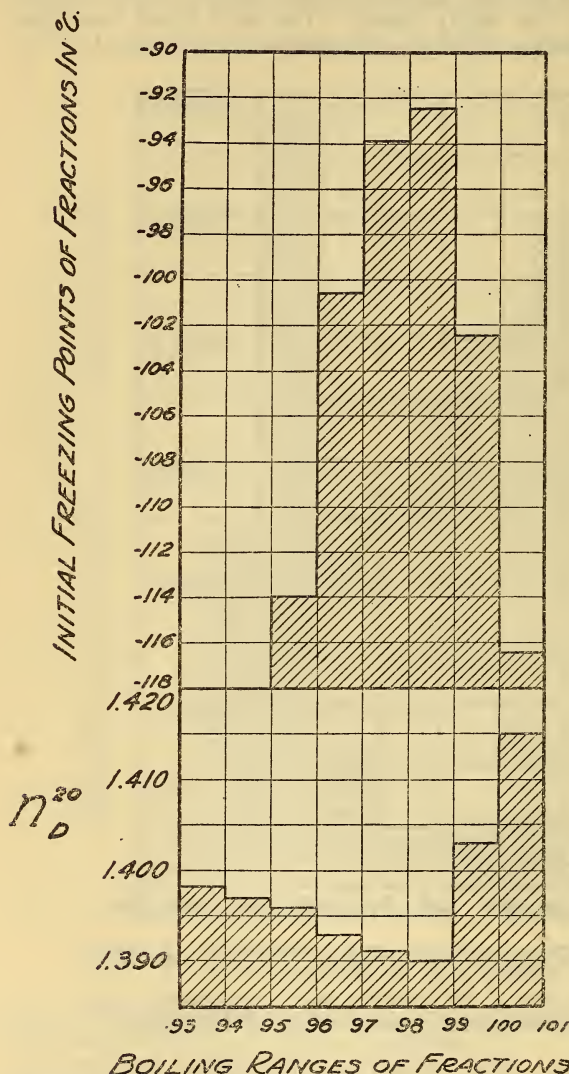


FIGURE 5.—The initial freezing points and the refractive indices of the fractions plotted against their boiling ranges

Separation of larger quantities of methylcyclohexane by this method was abandoned because at this point it was discovered that the reported constant-boiling minimum with *n*-heptane does not exist. This was confirmed in the following way: A sample of pure synthetic *n*-heptane was kept continuously boiling in a boiling-point apparatus of the Cottrell (27) type. As soon as a constant temperature reading was observed, small quantities of pure synthetic methylcyclohexane were introduced into the boiling-point apparatus through the condenser and the thermometer readings were recorded. The boiling point was determined for solutions of varying concentrations, but in no case could a lowering of the boiling point be observed.

3. Isolation of *n*-Heptane and Methylcyclohexane

The difference between the boiling points of methylcyclohexane and *n*-heptane (2.4° C.) is greater than the differences (0.35° and 1.05° C.) between the boiling points of the corresponding constant boiling mixtures of the respective hydrocarbons with methyl or ethyl alcohol (28). Consequently, a greater separation of these hydrocarbons should be expected by ordinary distillation than by distillation after admixture with the lower alcohols.

Accordingly, the fractions containing the *n*-heptane and the methylcyclohexane were subjected to careful distillations in a 35-foot column (18) packed with jack chain. These distillations were made at a rate of about 1 ml per minute and at a 10:1 reflux ratio. Five charges of about 2 liters each of the 98° to 99° C. cuts were put into the still and each charge was separated by distillation into about 30 fractions. For each of these 150 fractions, the refractive index, the boiling point, and, in most cases, the freezing point were determined. The lower boiling fractions from these distillations which had substantially the same refractive indices as pure *n*-heptane and freezing points not more than 0.5° below the freezing point of this hydrocarbon, were mixed. Two liters of this mixture were redistilled and yielded practically pure *n*-heptane.

The higher-boiling fractions from the above-mentioned five distillations had refractive indices and freezing points near those of methylcyclohexane and were mixed for further distillation. As a result of these distillations nearly pure methylcyclohexane was obtained.

In order to remove some of the last traces of impurities from the *n*-heptane, a 1,000 g sample of this material was subjected to a chlorosulphonic-acid treatment. As a result of this treatment and a subsequent distillation through a 30-plate column, heptane with a freezing point of -90.6_2 ° C. was obtained.

Another sample of the heptane material (with a boiling point 98.4° and a refractive index $n_D^{20} = 1.3878$) as well as some of the best fractions of the methylcyclohexane were subjected to further purification by equilibrium melting with the aid of the centrifuge. As an illustration of the separations which were obtained with the aid of the centrifuge, the results of two different fractionations of *n*-heptane are shown in Table 1. Some additional physical constants of the fraction with freezing point -90.66 are given in Table 2.

TABLE 1.—Some of the results obtained by submitting *n*-heptane samples of different degrees of purity to fractionations by centrifuging the crystals

	Volume	Freezing point	Purity
	<i>ml</i>	<i>°C.</i>	<i>Mole per cent</i>
Fractionation of <i>n</i> -heptane of low purity:			
Original material.....	500	−93.99	83.9
First fraction.....	107	−95.59	77.1
Second fraction.....	144	−95.44	77.7
Third fraction.....	113	−93.81	84.7
Fourth fraction.....	49	−92.21	92.2
Fifth fraction.....	73	−90.91	98.5
Fractionation of <i>n</i> -heptane of fairly high purity:			
Original material.....	225	−90.96	98.3
First fraction.....	50	−91.17	97.2
Second fraction.....	40	−90.99	98.2
Third fraction.....	70	−90.91	98.5
Fourth fraction.....	50	−90.66	99.8

4. DETERMINATION OF THE FREEZING POINT-COMPOSITION DIAGRAM OF THE BINARY SYSTEM: *n*-HEPTANE-METHYLCYCLOHEXANE

In order to be able to determine the approximate composition of the fractions shown in Figure 4, the freezing point-composition diagram for the system: *n*-heptane-methylcyclohexane was determined. For this purpose synthetic mixtures of known composition of *n*-heptane and methylcyclohexane were made up.⁸ The refractive index and the initial freezing point of each mixture were determined. The results are shown in Figure 6. It will be noted that the eutectic mixture of *n*-heptane and methylcyclohexane corresponds to about 93 weight per cent of methylcyclohexane and freezes at about −130.3° C.

IV. DISCUSSION OF THE RESULTS

In Table 2 a comparison is given between the physical constants of the best samples of *n*-heptane obtained in this work and the constants of *n*-heptane determined by other investigators.

TABLE 2.—Physical constants of *n*-heptane

<i>n</i> -heptane C ₇ H ₁₆	d_4^{20}	n_D^{20}	Boiling point (corrected)	Freezing point (in dry air)	Critical solution temperature in aniline	Molecular weight
			<i>°C.</i>	<i>°C.</i>	<i>°C.</i>	
Hicks-Bruun and Bruun:						
1. Obtained by distillation.....	^a 0.68437	^b 1.3877	98.4	−90.81	^d 70.0	^c 100.1
2. Obtained by chlorosulphonic acid treatment.....	^a .68365	^b 1.3877	98.4	−90.62	^d 70.0	^c 100.1
3. Obtained by centrifuging the crystals.....	^a .68376	^b 1.3877	98.4	−90.66	^d 70.0	^c 100.1 (theoretical 100.12)
Shepard, Henne, and Midgley (10).....	.68378	1.38775	98.38	−90.65	69.9	-----
Edgar and Calingaert (29).....	.6836	1.38777	98.4	−90.5	70.0	-----

^a Determined by the section of capacity and density of this bureau.

^b Determined by L. W. Tilton, of the optical division of this bureau.

^c The value for the freezing point of this sample was checked by B. J. Mair by means of a platinum resistance thermometer.

^d The weight percentage of *n*-heptane in the mixture giving its critical solution temperature with aniline was found to be approximately 45. Shepard, Henne, and Midgley (11) report about 66 weight per cent.

* For method see M. M. Hicks-Bruun, B. S. Jour. Research, vol. 5, p. 575, 1930.

⁸ The methylcyclohexane was obtained from the Bureau International des Etalons Physico-Chimiques and the *n*-heptane from the Ethyl Gasoline Corporation. The source of the latter was Jeffrey's pine.

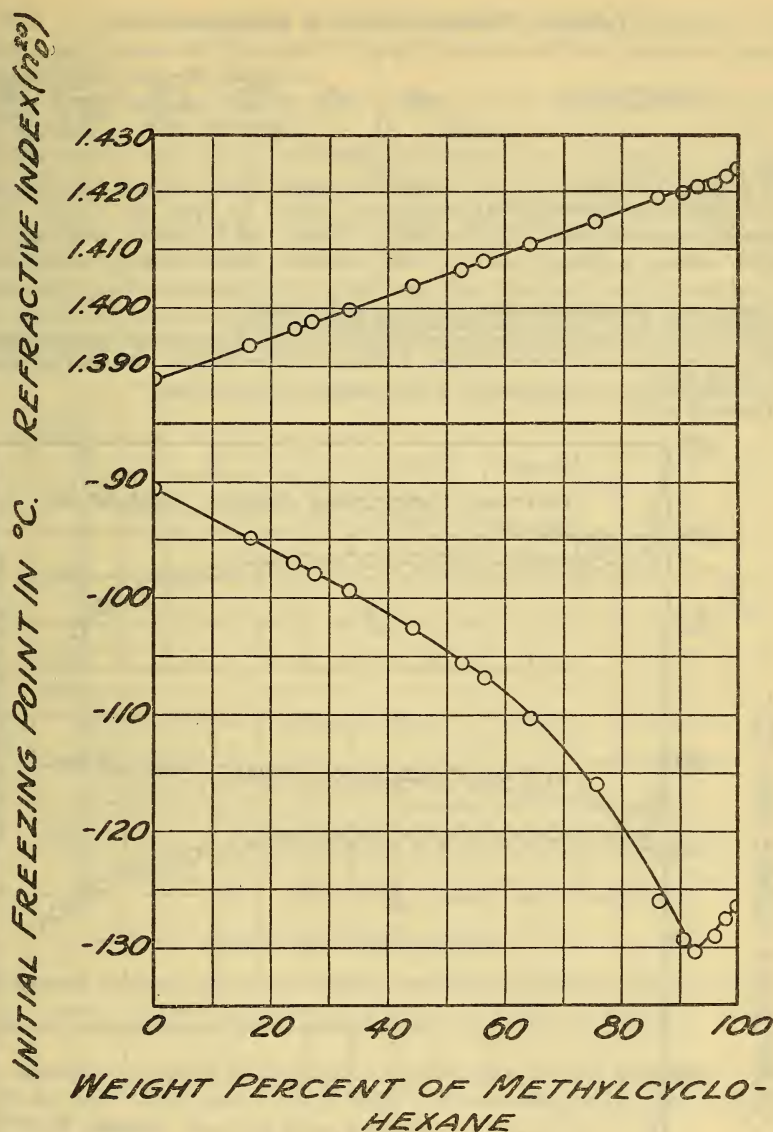


FIGURE 6.—The phase equilibrium diagram for the condensed system *n*-heptane-methylcyclohexane

The upper curve shows the refractive index (n_D^{20}) plotted against the composition of the synthetic mixture
In the lower graph the freezing point of the mixture is plotted against the composition.

TABLE 3.—Physical constants of methylcyclohexane

Methylcyclohexane C_7H_{14}	d_4^{20}	n_D^{20}	Boiling point (cor- rected)	Freezing point (in dry air)	Critical solution tempera- ture in aniline	Molecu- lar weight ⁵
Hicks-Bruun and Bruun:			$^{\circ}C.$	$^{\circ}C.$	$^{\circ}C.$	
1. Obtained by distillation.....	¹ 0.76918	² 1.4234	100.8	³ -126.53	41.0	— 498.1
2. Purified by centrifuging the crys- tals.....	¹ .76925	² 1.4234	100.8	³ -126.44	41.0	— 498.1
Timmermans and Martin (30).....	.76929	1.423	101.2	-126.4	41	-----
Int. Crit. Tables, vol. 1, p. 214.....	.764	1.4235	100.8	-126.4	-----	-----

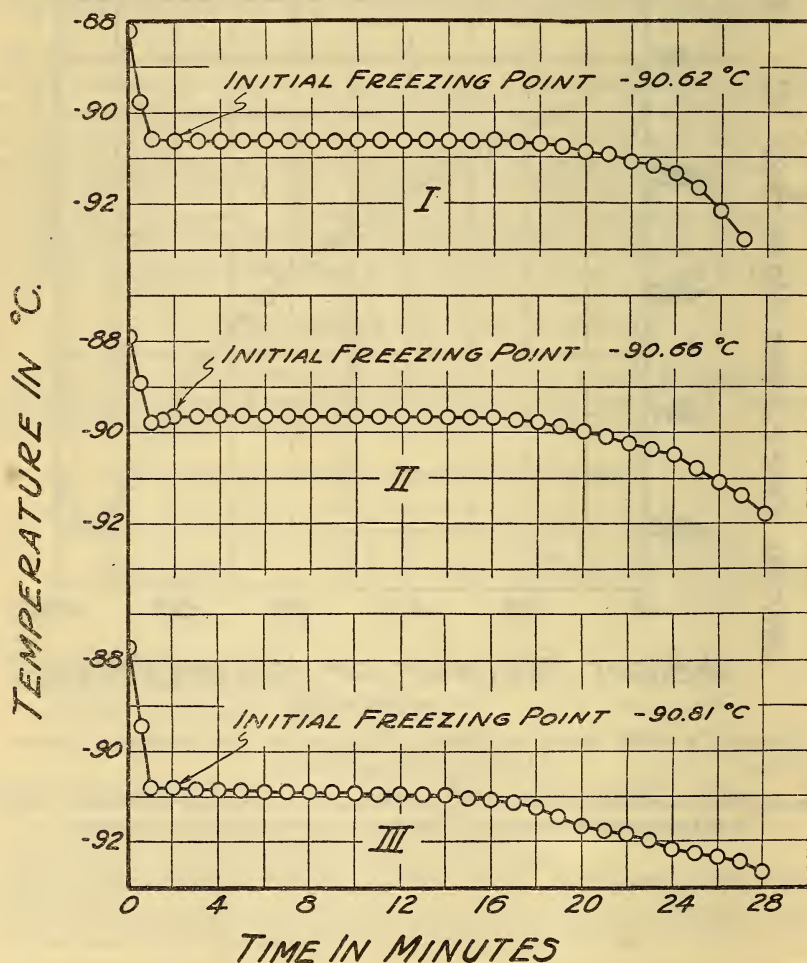
¹ Determined by the section of capacity and density of this bureau.² Determined by L. W. Tilton, of the optical division of this bureau.³ The freezing points on these samples were compared with a sample of pure synthetic methylcyclohexane obtained directly from the International Bureau des Étalons Physico-Chimique. The latter was found to freeze at $-126.40^{\circ}C.$ ⁴ For method see M. M. Hicks-Bruun, B. S. Jour. Research vol. 5, p. 575, 1930.⁵ Theoretical 98.108.

FIGURE 7.—Time-temperature cooling curve for the isolated *n*-heptane
 Curve I refers to *n*-heptane obtained by treatment with chlorosulphonic acid. Curve II refers to *n*-heptane purified by equilibrium melting and centrifuging. Curve III refers to *n*-heptane obtained by distillation.

The physical constants of the isolated methylcyclohexane, together with some of the most reliable values for the synthetic hydrocarbon, are given in Table 3.

The time-temperature freezing curves of the isolated hydrocarbons are shown in Figures 7 and 8. In reference to Figure 8 it may be well to point out that methylcyclohexane, on account of its high viscosity at low temperatures, exhibits a marked tendency to supercool. Since its heat of fusion is comparatively small, caution must be observed to avoid too much supercooling, in order that the temperature of the crystals may rise to the true freezing point. However, crystallization of the sample can be effected readily, either by the usual method of adding a few solid crystals when the temperature of the liquid is slightly below the freezing point, or by first freezing

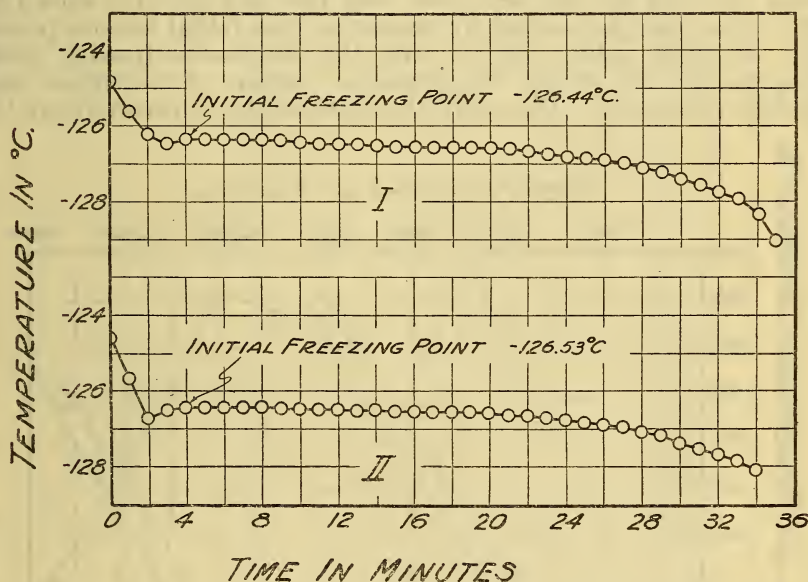


FIGURE 8.—Time-temperature cooling curve for the isolated methylcyclohexane

Curve I refers to methylcyclohexane purified by equilibrium melting and centrifuging. Curve II refers to methylcyclohexane obtained by distillation.

the fraction and then allowing it to melt slowly until almost all of the crystals have disappeared, and finally proceeding with the cooling in the usual manner.

The infra-red absorption spectra of the isolated hydrocarbons are shown in Figures 9 and 10. These were determined by U. Liddel, of the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture.

The purity of the best samples of *n*-heptane and methylcyclohexane isolated was calculated from their freezing points and the known values (31) of their heats of fusion (33.7 and 16.2 calories per gram, respectively). The results of these calculations are shown in Table 4.

TABLE 4

	Calculated purity
<i>n</i> -heptane purified by centrifuging the crystals.....	99.8
<i>n</i> -heptane purified by chlorosulphonic acid treatment.....	100.0
<i>n</i> -heptane isolated by distillation.....	99.0
Methylcyclohexane purified by centrifuging the crystals.....	99.8
Methylcyclohexane isolated by distillation.....	99.5

In order to compute the approximate quantities of *n*-heptane and methylcyclohexane which are present in the crude petroleum the reader is referred to Figure 4. The compositions of three large fractions (98° and 99°, 99° and 100°, and 100° and 101° C.) shown in this figure were determined by correlating their initial freezing points and refractive indices (fig. 5) with the composition-freezing point diagram (see fig. 6) for the synthetic mixture of *n*-heptane and methylcyclohexane. The results thus obtained are shown in Figure 11.

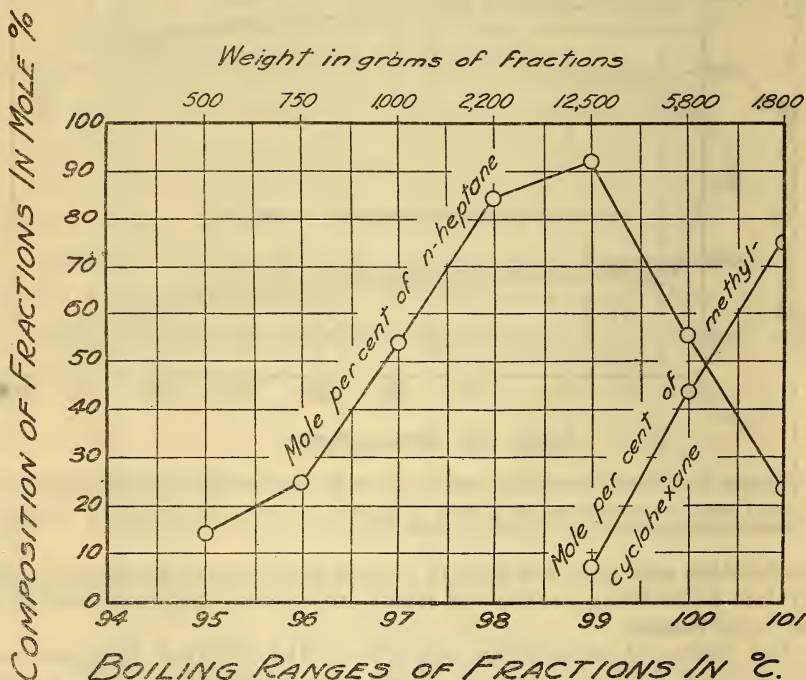


FIGURE 11.—Composition of the fractions shown in Figure 4

The mole percentage is plotted against the end temperature of each cut. The numbers at the top of the diagram show the weight in grams of each cut represented below

The fractions boiling between 95° and 98° C. were not binary mixtures, but contained lower boiling naphthenes and isomers of heptane. The mole per cent of *n*-heptane contained in these fractions has been calculated from their initial freezing points.

It was estimated from the results of further distillation that these fractions and the smaller fractions boiling between 93° and 95° contained about 2,700 g of *n*-heptane and 100 g of methylcyclohexane.

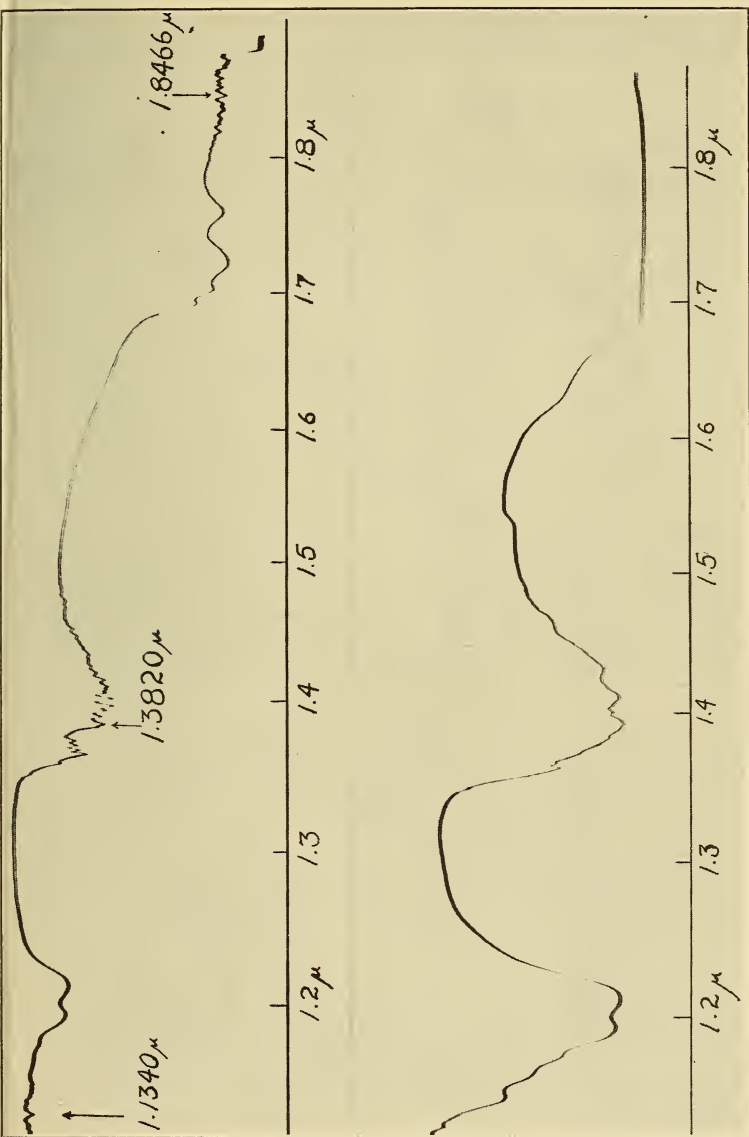


FIGURE 9.—The infra-red absorption spectrum of the isolated *n*-heptane

These curves are the energy transmission lines of the emission of a tungsten filament lamp through 1 mm and 1 cm cell thicknesses, respectively, of normal heptane, automatically recorded by an infra-red spectrograph in the region from 1 to 2 μ . These curves show the absorption of the compound at the first and second overtone frequencies of the 3.4 μ fundamental of hydrocarbon absorption at 1.73 μ and 1.20 μ and the combination band of this fundamental with another near 6 μ at 1.42 μ , besides the absorption of the water vapor necessarily present in the light path which is quite apparent as the fine band absorption and strong bands of which are indicated by the arrows. These spectra fit in nicely with the series of normal aliphatic hydrocarbon spectra studied by F. S. Brackett (Proc. National Acad. Sci., vol. 14, p. 861 (1928)). The records were taken with an effective slit width of approximately 20 Å. Measured by U. Liddel, of the Fixed Nitrogen Research Laboratory, United States Department of Agriculture.

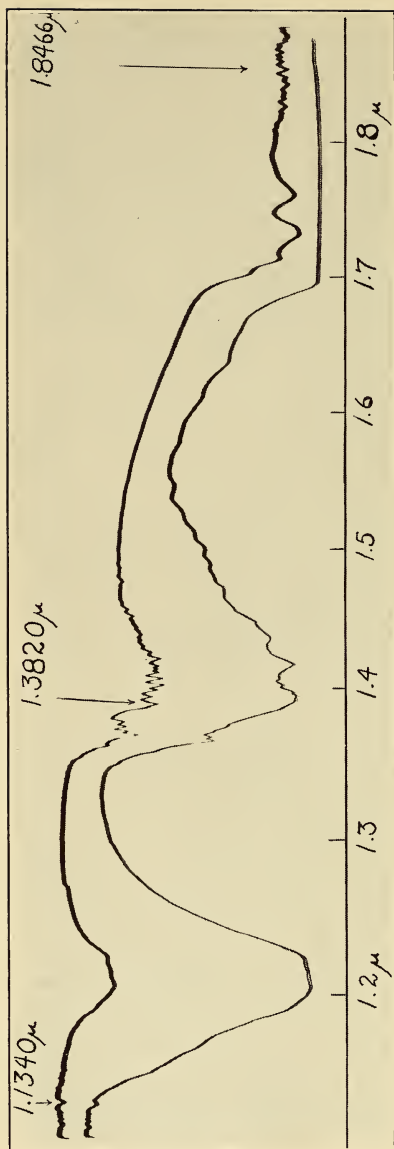


FIGURE 10.—*The infra-red absorption spectrum of the isolated methylcyclohexane*

The upper and the lower curves represent the transmission lines of the emission of a tungsten filament lamp through 1 mm and 1 cm cell thicknesses, respectively, of methylcyclohexane automatically recorded by an infra-red spectrograph in the region from 1 to 2 μ . These curves show the absorption of the compound at the first and second overtone frequencies of the 3.4 μ fundamental of hydrocarbon absorption at 1.74 μ and 1.21 μ and the combination band of this fundamental with another near 6 μ at 1.42 μ , besides the absorption of the water vapor necessarily present in the light path which is quite apparent as the fine band absorption and strong bands of which are indicated by the arrows. The records were taken with an effective slit width of approximately 20 A. Measured by U. Liddel, of the Fixed Nitrogen Research Laboratory, United States Department of Agriculture.

The other constituents of these fractions have boiling points of about 92° C. and are being further investigated. It should be noted that it was impossible to obtain the freezing points for the fractions with boiling ranges below 94.5° C. as these form glasses when cooled to low temperatures. This phenomenon has been found previously to be associated with the fact that isoparaffins and isonaphthenes, even when present in small quantities, often tend to cause abnormal supercooling or to prevent the crystallization of a mixture altogether.

It was concluded that the following values are a conservative estimate of the quantities of the hydrocarbons in the fractions shown in Figure 3:

<i>n</i> -heptane.....	17,800 ^g
methylcyclohexane.....	° 6,000

Based upon the crude petroleum (600 gallons, specific gravity 0.9) it is estimated that not less than 0.9 per cent of *n*-heptane and not less than 0.3 per cent of methylcyclohexane is present.

From a motor fuel standpoint it is well known that *n*-heptane, because of its poor detonation characteristics, is an undesirable constituent of the gasoline fraction. Consequently, the antiknock properties of this fraction could be improved if most of the *n*-heptane were removed by fractional distillation. This procedure could be applied to those petroleum of which the 98° and 99° C. cut consists mainly of *n*-heptane. A partial utilization of the heptane fraction could probably be found, if it were first purified by subjecting it to about two treatments with chlorosulphonic acid and a subsequent fractional distillation. In this way *n*-heptane of sufficiently high purity for antiknock standards could be obtained. The manufacturing cost of the *n*-heptane would probably be low enough to permit the use of this hydrocarbon as a constituent not only of the present-day antiknock standards, but also of the more widely used secondary standards.

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VI. BIBLIOGRAPHY

1. C. Schorlemmer, *J. Chem. Soc.*, vol. 15, p. 419, 1863. *Ber.*, vol. 4, pp. 395, 565, 1871; vol. 5, p. 297, 1872; vol. 6, p. 74, 1873; vol. 7, p. 1793, 1874.
2. E. Beilstein and A. Kurbatoff, *Ber.*, vol. 14, p. 1620, 1881.
3. K. Charitschkow, *Chem.-Ztg.*, vol. 26, p. 573, 1902. *Chem. Zentr.*, vol. 2, pp. 474, 920, 1899.
4. See references cited in Engler-Höfer, *Das Erdöl*, vol. 1, p. 244, 1919. S. Hirzel, Leipzig.
5. C. M. Warren, *Proc. Am. Acad. Arts Sci.*, vol. 27, p. 77, 1892.
6. C. F. Mabery, *Proc. Am. Acad. Arts Sci.*, vol. 31, p. 56, 1895.
7. R. P. Anderson and A. M. Erskine, *Ind. Eng. Chem.*, vol. 16, p. 266, 1924.
8. G. G. Brown and A. R. Carr, *Ind. Eng. Chem.*, vol. 18, p. 721, 1926.
9. F. E. Francis and S. Young, *J. Chem. Soc.*, vol. 73, p. 920, 1898.
10. A. F. Shepard, A. L. Henne, and T. Midgley, jr., *J. Am. Chem. Soc.*, vol. 53, p. 1948, 1931.

* Some additional quantities of methylcyclohexane will be found in the fractions distilling above the boiling range of the material used for the present investigation. Because of the comparatively small amounts of material boiling between 100° and 104° C. these additional quantities of methylcyclohexane will not materially change the percentage value of this hydrocarbon in the crude petroleum.

11. O. Aschan, *Ber.*, vol. 31, p. 1801, 1898.
12. Br. Lachowicz, *Ann.*, vol. 220, pp. 188-206, 1883.
13. K. Charitschkow, *Chem. Zentr.*, vol. 2, p. 920, 1899.
14. S. Young, *J. Chem. Soc.*, vol. 73, pp. 906-920, 1898.
15. P. Poni, *Chem. Zentr.*, vol. 2, p. 452, 1900.
16. C. F. Mabery and O. J. Sieplein, *Proc. Am. Acad. Arts Sci.*, vol. 36, p. 275, 1901.
17. W. C. Markownikoff, *Chem. Zentr.*, vol. 1, p. 1345, 1904.
18. J. H. Bruun and S. T. Schicktanz, *B. S. Jour. Research*, vol. 7, pp. 851-882, 1931.
19. J. H. Bruun, R. T. Leslie, and S. T. Schicktanz, *B. S. Jour. Research*, vol. 6, p. 363, 1931.
20. C. W. Kanolt, *B. S. Sci. Papers* No. 520.
21. E. W. Washburn, J. H. Bruun, and M. M. Hicks, *B. S. Jour. Research*, vol. 2, pp. 469 and 484, 1929.
22. J. H. Bruun and M. M. Hicks-Bruun, *B. S. Jour. Research*, vol. 7, p. 608, 1931.
23. M. Lecat, *Rec. trav. Chim.*, vol. 45, 620, 1926.
24. J. H. Bruun and M. M. Hicks-Bruun, *B. S. Jour. Research*, vol. 5, pp. 933-942, 1930.
25. J. H. Bruun and M. M. Hicks-Bruun, *B. S. Jour. Research*, vol. 6, pp. 869-880, 1931.
26. R. T. Leslie, *B. S. Jour. Research*, vol. 8, May, 1932.
27. F. G. Cottrell, *J. Am. Chem. Soc.*, vol. 41, p. 721, 1919.
28. M. Lecat, *Ann. Soc. Sci. Bruxelles, B*, vol. 48, pp. 107-108, 1928.
29. G. Edgar and G. Calingaert, *J. Am. Chem. Soc.*, vol. 51, p. 1544, 1929.
30. J. Timmermans and F. Martin, *J. chim. phys.*, vol. 23, p. 763, 1926.
31. G. S. Parks and H. M. Huffman, *Ind. Eng. Chem.*, vol. 23 p. 1138, 1931.

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